

(3) climatic warming, perhaps coeval to the termination of the Sun's T Tauri phase, and resulting poleward latitudinal shift of the zones of preserved ground ice.

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**A CARBON DIOXIDE/METHANE GREENHOUSE ATMOSPHERE ON EARLY MARS.** L. L. Brown and J. F. Kasting, Department of Geosciences, Pennsylvania State University, University Park PA 16802, USA.

One explanation for the formation of fluvial surface features on early Mars is that the global average surface temperature was maintained at or above the freezing point of water by the greenhouse warming of a dense CO<sub>2</sub> atmosphere [1]; however, Kasting [2] has shown that CO<sub>2</sub> alone is insufficient because the formation of CO<sub>2</sub> clouds reduces the magnitude of the greenhouse effect. It is possible that other gases, such as NH<sub>3</sub> and CH<sub>4</sub>, were present in the early atmosphere of Mars and contributed to the greenhouse effect. Kasting et al. [4] investigated the effect of NH<sub>3</sub> in a CO<sub>2</sub> atmosphere and calculated that an NH<sub>3</sub> mixing ratio of  $\sim 5 \times 10^{-4}$  by volume, combined with a CO<sub>2</sub> partial pressure of 4-5 bar, could generate a global average surface temperature of 273 K near 3.8 b.y. ago when the fluvial features are believed to have formed. Atmospheric NH<sub>3</sub> is photochemically converted to N<sub>2</sub> by ultraviolet radiation at wavelengths shortward of 230 nm; maintenance of sufficient NH<sub>3</sub> concentrations would therefore require a source of NH<sub>3</sub> to balance the photolytic destruction. We have used a one-dimensional photochemical model to estimate the magnitude of the NH<sub>3</sub> source required to maintain a given NH<sub>3</sub> concentration in a dense CO<sub>2</sub> atmosphere [5]. We calculate that an NH<sub>3</sub> mixing ratio of 10<sup>-4</sup> requires a flux of NH<sub>3</sub> on the order of 10<sup>12</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>. This figure is several orders of magnitude greater than estimates of the NH<sub>3</sub> flux on early Mars; thus it appears that NH<sub>3</sub> mixed with CO<sub>2</sub> is not enough to keep early Mars warm.

We are currently using a one-dimensional radiative-convective climate model to determine the greenhouse effect of CH<sub>4</sub> in a CO<sub>2</sub> atmosphere. Atmospheric CH<sub>4</sub> would have a longer lifetime than NH<sub>3</sub> because CH<sub>4</sub> photolysis occurs only at wavelengths shortward of 145 nm, whereas NH<sub>3</sub> is photolyzed out to 230 nm. Hydrocarbon aerosols, which are formed as a product of CH<sub>4</sub> photolysis, are highly absorbent and may have provided a UV shield that would have lengthened the photochemical lifetime of CH<sub>4</sub> itself, as well as other hydrocarbon gases and NH<sub>3</sub>. The greenhouse effect resulting from the combination of these gases and particles could conceivably have raised the mean global surface temperature of Mars to near the H<sub>2</sub>O freezing point. A combination of radiative-convective climate modeling and photochemical modeling should show whether this idea is feasible and how large a CH<sub>4</sub> source would be needed.

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**OXIDATION OF DISSOLVED IRON UNDER WARMER, WETTER CONDITIONS ON MARS: TRANSITIONS TO PRESENT-DAY ARID ENVIRONMENTS.** R. G. Burns, Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge MA 02139, USA.

**Introduction:** The copious deposits of ferric-iron assemblages littering the surface of bright regions of Mars indicate that efficient oxidative weathering reactions have taken place during the evolution of the planet. Because the kinetics of atmosphere-surface (gas-solid) reactions are considerably slower than chemical weathering reactions involving an aqueous medium, most of the oxidation products now present in the martian regolith probably formed when groundwater flowed near the surface. This paper examines how chemical weathering reactions were affected by climatic variations when warm, wet environments became arid on Mars. Analogies are drawn with hydrogeochemical and weathering environments on the Australian continent where present-day oxidation of iron is occurring in acidic groundwater under arid conditions.

**Background:** Chemical weathering reactions of basaltic rocks are facilitated in aqueous solutions. Several stages are involved [1-3], including (1) dissolution of basaltic glass, iron sulfides, and ferromagnesian silicate minerals, which deliver soluble Mg<sup>2+</sup>, Fe<sup>2+</sup>, Ca<sup>2+</sup>, silica, etc., to groundwater; (2) ferrololysis, during which oxidation of dissolved Fe<sup>2+</sup> occurs, producing soluble Fe<sup>3+</sup> ions, which are eventually hydrolyzed to Fe(III) oxyhydroxy- and hydroxysulfato gels and colloids; and (3) precipitation of poorly crystalline ferric oxides, oxyhydroxides, and sulphate minerals, as well as clay silicate and evaporite minerals, in depositional environments such as the martian regolith.

Rates of chemical weathering of Fe<sup>2+</sup>-bearing minerals in aqueous environments that are applicable to the martian surface have been estimated from experimental data for basaltic minerals [2,3]. Reaction rates are strongly influenced by acidity or pH [4,5], as well as salinity or ionic strength [6], concentration of dissolved O in aerated groundwater [7,8], and temperature [7,8]. In acidic groundwater (pH < 4.5), silicate minerals dissolve rapidly, but rates of oxidation of aqueous Fe<sup>2+</sup> ions are very slow, particularly in brines at low temperatures.

For example, rates of dissolution of olivine and pyroxenes range from about 1400 ppm Fe m<sup>-2</sup> yr<sup>-1</sup> (pH 2 at 25°C) to 2 × 10<sup>-2</sup> ppm Fe m<sup>-2</sup> yr<sup>-1</sup> (pH 6 at 0°C). In acidic ice-cold saline solutions (pH 4.5 at 0°C), dissolution rates are about 1 ppm Fe m<sup>-2</sup> yr<sup>-1</sup>. In such melt waters saturated with O in the present-day martian atmosphere (P<sub>O<sub>2</sub></sub> = 10<sup>-5</sup> bar), the rate of oxidation of dissolved Fe<sup>2+</sup> is also about 1 ppm Fe m<sup>-2</sup> yr<sup>-1</sup>. Rates of oxidation are much higher in near-neutral pH saline groundwater and brines; thus, for brines with ionic strengths of 1 to 5 molal, rates of oxidation range from 500 to 900 ppm Fe m<sup>-2</sup> yr<sup>-1</sup> (pH 6 at 0°C) to about 100 ppm Fe m<sup>-2</sup> yr<sup>-1</sup> (pH 6 at -25°C). Such relatively low rates of oxidation of aqueous Fe<sup>2+</sup> contrast with the very high values for terrestrial river water ( $\approx 1.8 \times 10^7$  ppm Fe m<sup>-2</sup> yr<sup>-1</sup> for pH 6 at 25°C), and for deep ocean bottom water ( $\approx 5 \times 10^6$  ppm Fe m<sup>-2</sup> yr<sup>-1</sup> for pH 8.2 at 2°C). On Mars, the rate of oxidation of dissolved Fe<sup>2+</sup> in aerated near-neutral pH saline solutions would exceed the rate of supply of dissolved Fe, except in very acidic groundwater.

Calculations indicate that the mixing ratio of O in the present-day martian atmosphere is not being regulated by the oxidation of

aqueous  $\text{Fe}^{2+}$  ions. In pH 6 saline waters at  $0^\circ\text{C}$ , rates of oxidation of dissolved  $\text{Fe}^{2+}$  would have to exceed  $14,000 \text{ ppm Fe m}^{-2} \text{ yr}^{-1}$  to maintain the  $\text{P}_{\text{O}_2}$  at  $10^{-5}$  bar relative to  $\text{P}_{\text{CO}_2} = 3.4 \times 10^4$  bar. If the  $\text{P}_{\text{CO}_2}$  was  $1000\times$  higher than present-day values (i.e.,  $\text{P}_{\text{CO}_2} = 0.35$  bar), a  $\text{P}_{\text{O}_2}$  of  $10^{-5}$  bar could be achieved, supporting the suggestion [e.g., 9] that atmospheric pressure was higher earlier in Mars' history. On the other hand, the comparatively high  $\text{P}_{\text{O}_2}$  of the martian atmosphere would effectively oxidize the high concentrations of  $\text{Fe}^{2+}$  ions that could be present in very acidic solutions if such groundwaters occurred on Mars.

**Generation of Acidic Groundwater:** Oxygen in subsurface groundwater is consumed by oxidation of iron sulfides (e.g.,  $\text{FeS}_2 + 7/2 \text{ O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{ SO}_4^{2-} + 2 \text{ H}^+$ ) and by oxidation of some of the  $\text{Fe}^{2+}$  ions (i.e.,  $\text{Fe}^{2+} + 1/4 \text{ O}_2 + 3/2 \text{ H}_2\text{O} \rightarrow \text{FeOOH} + 2 \text{ H}^+$ ) released during oxidation of sulfides and from dissolution of ferromagnesian silicates. Such ferrolysis reactions cause groundwater to become acidic, facilitating the dissolution of ferromagnesian silicates. Since  $\text{Fe}^{2+}$  ions are stabilized and are very slowly oxidized in low pH saline solutions, concentrations of dissolved ferrous iron increase (perhaps to as high as  $1000 \text{ ppm}$ ) and may persist indefinitely in acidic groundwater (now permafrost on Mars). Oxidation to insoluble nanophase ferric oxides, oxyhydroxides, and hydroxysulfate minerals would occur rapidly when melt waters become oxygenated in contact with the atmosphere and when acid-buffering reactions occurred involving the formation of clay silicates. Such clay silicates include authigenic Mg-Fe saponites, which are also precipitated from acidic brines, and residual montmorillonites derived from leached basaltic feldspars. Environments on the present-day martian surface that are capable of precipitating ferric-bearing assemblages are equatorial melt waters and regions where sublimation of permafrost has induced the oxidation of  $\text{Fe}^{2+}$  ions after they were released in evaporite deposits. Oxidative weathering reactions in arid environments might have been more prevalent earlier in the history of Mars, however, by analogy with unique terrestrial environments in Australia.

**Terrestrial Analogs:** On Earth, natural acidic groundwater systems are comparatively rare but occur, nevertheless, when water seeps through mined sulfide and coal deposits. Outflows of such acid mine drainage water are invariably associated with ochrous ferric-bearing assemblages. On a much larger scale, oxidative weathering associated with acidic groundwater is occurring across the southern half of the Australian continent [10].

In the southeastern part of Western Australia, deep weathering of basement igneous rocks in the Yilgarn Block comprising Archean komatiitic basalts has yielded saline groundwater systems, drainage of which in a semi-arid climate has resulted in extensive playas [10–15]. The discharging water contains high concentrations of dissolved Al, Si, and  $\text{Fe}^{2+}$ , oxidation and hydrolysis of which generates very acidic groundwater ( $\text{pH} \geq 2.8$ ), as a result of the ferrolysis reactions. The acidity prevents the precipitation of aluminosilicate clay minerals. Instead, jarosite [ $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ]-alunite [ $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ] assemblages are precipitated in the pH range 2.8–6 from solutions with ionic strengths ranging from 1 M to 5 M, occurring in evaporite deposits with gypsum and halite. Ferrihydrite, instead of jarosite-alunite assemblages, is deposited from groundwater depleted in dissolved K and Al. A similar situation may exist on Mars where groundwater associated with parent iron-rich komatiitic basaltic rocks may also have low Al and K contents.

Two stages were important in the development of the acidic hydrogeochemical and arid weathering environment of southern Australia. Initially, there were periods of laterization/ferric oxide deposition under a warm humid climate during the Tertiary. The laterite profiles are characterized by a surface duricrust of Fe and Al oxides over deep clay silicate zones depleted of alkali and alkaline Earth elements. Subsequently, periods of aridity and semi-aridity have continued to the present.

An explanation for the acidic saline groundwater systems on such a large scale and only in Australia lies in the recent climatic history of the continent. After the break from Antarctica began at 65 Ma, Australia moved into the subtropic region. The climate through the Eocene was humid and warm, much like that proposed on early Mars, and periods of laterization occurred. Laterite profiles became abundant in Western Australia on deeply weathered bedrock depleted in alkalis and alkaline earth elements, but enriched in Fe, Al, and Si. Little chemical weathering is now occurring on the Australian continent today due to arid conditions. However, periodic discharges of anoxic acidic groundwater into the arid environment and oxidation of the dissolved ferrous iron continue to generate ferric-bearing mineral assemblages in contact with the oxygenated atmosphere. A similar scenario may apply to the present-day surface of Mars, in which periodic precipitation of hydronium jarosite and ferrihydrite may be precursors to nanophase hematite identified in bright regions of the martian surface.

**Acknowledgments:** This research was supported by NASA grant no. NAGW-2220.

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N94-21664  
05-91 ABS ONLY 177595 p. 3  
**MARS: NOACHIAN HYDROLOGY BY ITS STATISTICS AND TOPOLOGY.** N. A. Cabrol and E. A. Grin, Laboratoire de Physique du Système Solaire, Observatoire de Paris-Meudon, 92190, France.

Discrimination between fluvial features generated by surface drainage and subsurface aquifer discharges will provide clues to the understanding of early Mars' climatic history. Our approach is to define the process of formation of the oldest fluvial valleys by statistical and topological analyses [1–3].

Formation of fluvial valley systems reached its highest statistical concentration during the Noachian Period. Nevertheless, they are a scarce phenomenon in martian history, localized on the cratered upland and subject to latitudinal distribution [1,4,5]. They occur sparsely on Noachian geological units with a weak distribution